

## MEASUREMENT OF THE HEAT CAPACITIES OF PURE AND MIXED REFRIGERANTS

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### ABSTRACT

A flow calorimeter was designed and built to measure the heat capacity of pure and mixed halogenated hydrocarbons in the liquid phase. The calorimeter is an electrically heated, coiled tube located inside a vacuum chamber in the water bath. The liquid under investigation is pumped by means of a syringe pump through the calorimeter and then collected in a pressure container located in dry ice to ensure a constant back pressure. The temperature difference is measured with a thermopile made of wire of 0.002 inch in diameter, and the flow rate is determined by weighing of the sample. The calorimeter was calibrated using water, refrigerant 11, refrigerant 22, and ethylene glycol. The measurement error is  $\pm 1\%$ . Results are reported for the pure refrigerants R114, R123, R142b and R152a, and the mixtures R22/R114, R22/R142b and R22/R152a.

### Introduction

Halogenated hydrocarbons are widely used as refrigerants in vapor compression systems for air-conditioning and heat pumping applications. The major draw back and limitation of any conventional system using a pure working fluid is the low Carnot efficiency and the severe capacity degradation under large temperature lift conditions. It is known that the use of working fluid mixtures offers at least the potential to reduce or sometimes even to eliminate these shortcomings.

In order to design vapor compression systems that are able

to take advantage of refrigerant mixtures the thermodynamic and transport properties of the working fluid combination have to be known. Considerable progress has been made toward this goal by several groups of researchers [1,2,3]. The work reported here is a contribution to the ongoing development of an equation of state that allows the evaluation of vapor-liquid equilibrium (VLE) data and single phase properties (pressure, temperature, volume and liquid and vapor concentration) in a thermodynamically consistent way [4]. Further, the equation of state allows the calculation of enthalpy and entropy. Due to the mathematical relationship between thermodynamic properties the enthalpy is obtained as a derivative of properties calculated by the equation of state. The single phase heat capacity is obtained as a second derivative. Consequently, any uncertainty of the measured VLE-data on which the equation of state parameters are based, is amplified in the heat capacity. In order to maximize the accuracy of the equation of state it was desired to experimentally determine the heat capacity of refrigerant mixtures in the liquid phase. Emphasis is placed on the liquid phase for the following reason. The equation of state requires the ideal gas heat capacity of the fluids for enthalpy calculations. This value is readily available from literature. Since measured caloric parameters for the gas phase are known, even for infinite dilution, the specific heat of the real gas can be computed rather accurately. However, the ideal gas heat capacity is not a good indicator for the heat capacity of the

liquid phase, thus it must be obtained by measurement.

### **State of the Art Heat Capacity Measurements**

For the design of the experiment a literature review was conducted in order to determine the most suitable calorimeter type for this task. It was concluded that a flow calorimeter is the most appropriate instrument. Several designs are reported [5,6,7,8,]. A common feature of all these instruments is that the fluid under investigation flows through a small diameter tube and is electrically heated in a well controlled thermal environment. This is achieved by single or multiple thermal shields and by accurate temperature control.

### **Experimental Facility**

Figure 1 shows a schematic of the experimental facility. The fluid under investigation is pumped by means of a syringe pump which provides a constant flow rate of up to  $6 \text{ cm}^3/\text{min}$  and has a capacity of  $500 \text{ cm}^3$ . The fluid enters a preheater, consisting of an electrically heated brass block in which 3 m of 1.5875 mm (1/16") diameter stainless steel tubing is embedded, where it is preheated to a temperature close to the calorimeter temperature. Then the fluid enters a second heat exchanger, a 5 m long coil of stainless steel tubing, followed by 4 m coiled copper tube, both of which are located in the same water bath as the calorimeter itself. The water bath temperature is controlled to within  $0.004^\circ\text{C}$ . Here the fluid is further heated to the

temperature of the calorimeter. The calorimeter is again a stainless tube coil of 2 m length, 1.5875 mm (1/16") OD located inside a vacuum chamber which in turn is located inside the water bath. The vacuum was maintained at 8 micron.

Originally a heater wire was wrapped on the outside of this capillary. The first series of test were conducted with this design. After repairs became necessary the external heater was replaced with a heater wire on the inside of the capillary which ran along its full length and reduced the heat loss from the heater to the surroundings. The temperature difference of the fluid between inlet and outlet is measured by a three-junction copper-constantan thermopile. For redundancy the temperature differences between the heater inlet and the water bath, and the heater outlet and the water bath were measured as well. After passing through the calorimeter the fluid passes a back pressure regulator and is finally collected in one of two sample cylinders which are cooled in dry ice. The first cylinder collects fluid while the system is approaching steady state, the second while a measurement is actually being performed. In this way the flow rate can be determined in two ways, by the pump setting and the weight of the sample used during a test. The heat input to the electric heater inside the calorimeter is controlled so that the temperature increment of the fluid leaving (compared to the temperature at the inlet) is 1 K (2 K for the first set of tests) at all times. Then the heat capacity is determined by the following equation:

$$C_p = \frac{P}{m \cdot (T_{out} - T_{in})}$$

where  $C_p$  represents the heat capacity,  $P$  the power input by the heater inside the calorimeter,  $m$  the mass flow rate, and  $T_{out}$  and  $T_{in}$  are the outlet and inlet temperatures. The power input is measured with a four line connection to the power supply with an accuracy of 0.05%. The mass flow rate is determined by weighing the sample cylinder before and after the test and checked with the volume flow rate setting of the pump. The accuracy of the mass flow rate is typically 0.5%. The temperature difference is determined by a three junction thermopile which is manufactured from copper and constantan wires of 0.0508 mm (0.002") diameter. The thermocouple wires were not calibrated individually since the calorimeter had to be calibrated as a whole. The accuracy of the temperature measurement is 0.008 C. The overall accuracy of the specific heat measurements therefore should be  $\pm 1\%$ .

#### **Measurement Procedure**

In order to conduct a test the syringe pump is charged with the fluid under investigation. In case of pure fluids with boiling points above room temperature, the pump was filled by sucking the liquid from a container open to the atmosphere.

In the case of low boiling fluids a pressure container was filled with the fluid or mixture under investigation and the liquid phase transferred from a valve located at the liquid phase end of the container while the piston of the pump moved from the

upper dead end to the lower. In order to prevent cavitation it was helpful to add helium to the vapor phase, ensuring that the liquid was subcooled. For low pressure fluids the piston moved at high speed, completing the filling process in about 10 minutes. For the high pressure fluids the piston had to move at a much slower speed, so that the gear ratio of the pump gear box still allowed the motor to control the fluid flow. If higher speeds were attempted, the pressure of the fluid would simply push the piston uncontrollably and jam it into the lower dead end. Thus, to charge high pressure fluids took typically one to two hours. The refrigerants were used as they were supplied by the manufacturer. Mixtures were prepared on a weight basis, and the refrigerants were mixed in a pressure container prior to charging the pump.

The water used in the experiment was distilled and degassed by boiling for thirty minutes. The glycol was also used as supplied by the manufacturer, however great care was taken to remove all moisture by boiling the fluid for two to three hours monitoring the boiling temperature. When the boiling point of the pure fluid was reached the glycol was stored in a sealed container and from that charged to the pump when room temperature was reached.

When the pump was charged, the calorimeter temperature had obtained its set value (which usually was maintained for weeks), and the insulation vacuum had the value of eight micron, then a test was initiated by turning on the pump. All measurements were

conducted at a constant flow rate setting of  $2 \text{ cm}^3/\text{min}$ . At first the flow was directed into a sample container that collects the sample during the start-up phase. While the system approached equilibrium the pressure was adjusted to the desired value with the back pressure regulator in conjunction with a needle valve. In addition the electric heater was turned on and controlled to achieve the desired temperature rise of the sample. Typically, it took typically one to two hours to achieve steady state. After steady state was reached the sample container collecting the fluid was changed to the one collecting the exact amount of sample during the measurement period itself. The duration of the test was clocked by the data acquisition system, usually thirty minutes. During this time a scan was performed every minute and all data collected by the data acquisition system were stored. After completion of the test the liquid stream was again redirected into the first sample container. The flow rate was determined from the amount of liquid collected and the duration of the test.

Besides the calibration additional tests were done where the fluid was passed through the test section without any heat input. Ideally the fluid temperature would not change. However a slight, reproducible increase or decrease of up to  $0.05 \text{ C}$  in the temperature between inlet and outlet was observed depending on the fluid. It is assumed that this temperature change is caused by the pressure drop the fluid experiences in the test section. This deviation was accounted for in the data evaluation.

## Results and Discussion

Tests were conducted for a fixed flow rate of  $200 \text{ cm}^3/\text{hr}$  and with a temperature increase set to 1 K (2 K for the first series of tests, listed with a temperature of 56.0 C in the tables). Every data point reported here was measured at least five times to ensure reproducibility. For the high temperatures the pressure is 3790 kPa (550 psi) and 2410 kPa (350 psi) for the low temperatures. The results for repeated measurements deviated from each other by typically 1%. The calorimeter was calibrated with water, refrigerant 11, refrigerant 22 and glycol at each temperature level at which tests were performed. Figures 2 through 5 show calibration curves for operating temperatures of 20.5 C, 37.5 C, 55.5 C and 56.0 C respectively. The experimentally determined specific heat is plotted vs. the literature values. The curve for 56 C was the first measured using the external heater and is based on a temperature difference of 2 K. Comparing this curve with the previous two shows that at 56 C the measured specific heat of water is in the range of  $5.6 \text{ kJ/kg/K}$ , while for the newer curves this value has improved to  $4.8 \text{ kJ/kg/K}$  due to the better controlled heat loss. This deviation is due to the fact that the calibration curve at 56 C (and all the tests at that temperature) were measured with a previous version of the calorimeter, where the heater wire was located on the outside of the tube coil and a temperature difference between inlet and outlet of 2 K was used. The higher



thermal losses from the heater contributed to an higher 'apparent' specific heat of water.

Although the calibration curves show a slight curvature, in the range of interest, indicated by the values for R22 and R11, they are fairly linear. Table 1 at the end of the report displays all measured data for the calibration runs. These data are shown after the curve fit for the calibration was applied. This is an indication for the quality and consistency of the curve fit. Comparing the numbers in Table 1 confirms that the curve fit through the calibration points reproduces the literature value quite well. For consistency it was decided that all calibrations would be on data provided by NEL [9].

The heat capacity of the liquid phase was measured for the following fluids and mixtures: R114, R123, R142b, R152a and the mixtures of R22/R114, R22/R142b, and R22/R152a. R22/R152a was added to the list later and its values are reported here for one temperature value (37.5 C) only. The values obtained for all pure fluids are reported in Table 2. This table also shows the fluids used for calibration together with the literature data the calibration was compared to.

While for R11 the data published by ASHRAE [10] and NEL agree quite well, we find a significant deviation for R22 of about 3% for the higher temperature. For R114 we find experimental values that are in good agreement with NEL's data and the data published by Sato [8], the most recent publication for this fluid, while the ASHRAE data seem to be 3% lower for the

low temperature and 3% higher for the high temperature. It should be noted that Sato's data were measured at 2000 kPa. However, for liquids the specific heat is not very dependent on pressure, so no distinction is made here between data taken for saturated or subcooled fluids. This is confirmed by Sato's data which span a pressure range up to 3000 kPa. For R123 the specific heat found here is 7.5% lower than reported by NEL over the entire temperature range. For R142b we find a value that reproduces ASHRAE data within 1% over the entire range. At 20.5 C the measured value is 6% lower than NEL's but they agree at 55.5 C. The measured specific heat for R152a at 20.5 C is 4% lower than NEL's data, and 1% lower than ASHRAE's value. At 37.5 C the value agrees with NEL and is 1% lower than ASHRAE.

All measured values were also compared to the data derived from the CSD equation of state [4]. For R11 the prediction is about 1 to 2% lower than the NEL value over the entire range, for R22 the deviation is about 4%, while for R114 good agreement within 1% is obtained. For R142b a 3% lower value is predicted at 20.5 C and the measured value is under predicted by 4% at 55.5 C. For 152a the equation consistently underpredicts the specific heat by up to 10%.

Figure 6 displays the measured specific heat vs. mixture concentration for R22/R114 for two temperature levels, the upper and lower limit of the range. In this figure the results of all measurements are plotted, indicating the range of uncertainty. For comparison the data obtained with the current version of the

CDS Equation of State (EOS) are plotted as well (continuous line in Figure 6). At the high temperature level, the measured data are consistently higher by up to 7% than predicted by the EOS. This holds for all mixture concentrations. At the low temperature level the EOS over predicts the specific heat for pure R114 by 1%, and under predicts it for pure R22 as discussed above. For R22 the 3% deviation between our results and the prediction are consistent with regard to the sign, but not so for R114. The heat capacity of R114 depends considerably stronger on temperature than expected according to the EOS. The deviation of the EOS values can be explained to some extent by the fact that the data available to date for R114 from ASHRAE do not agree with results obtained by Sato. The measured values of the mixture are slightly lower than for the mass-weighted average, which would be found on a straight line connecting the values for the two pure components.

Figure 7 shows the results obtained for R22/R142b, again for two temperature levels and based on weight concentrations and specific heat. Here we find again a deviation between the pure R22 and R142b data and the equation of state. The EOS underpredicts all specific heats by up to 5%.

Figure 8 shows the results for R22/R152a. Here only one temperature level is reported since this mixture was added later to the project. All measured values are consistently higher than predicted by the EOS. The maximum deviation is found for pure R152a of 10%.

In Table 3 the numerical values of the mixture measurements are reported.

### Conclusion

A flow calorimeter has been built and operated that allows the measurement of the heat capacities of subcooled liquids with an accuracy of approximately  $\pm 1.0\%$ . The specific heat of four pure fluids and three mixtures were measured. It is found that the CSD equation of state in its current version usually under predicts the liquid specific heat capacity of pure and mixed refrigerants. In the worst case by up to 10% for the mixture of R22/R152a. The best agreement is obtained for R22/R142b (5% under prediction).

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Table 1: Calibration Data

	20.5 C		37.5 C		55.5 C		56.0 C	
Fluid	Cp(e) J/gK	Cp(1) J/gK	Cp(e) J/gK	Cp(1) J/gK	Cp(e) J/gK	Cp(1) J/gK	Cp(e) J/gK	Cp(1) J/gK
H <sub>2</sub> O	4.183	4.183	4.180	4.180	4.182	4.182	4.183	4.183
Glycol	2.381	2.381	2.470	2.470	N/A		2.570	2.570
R22	1.247	1.247	1.320	1.320	1.496	1.496	1.500	1.505
R11	0.889	0.889	0.897	0.897	0.923	0.922	0.927	0.923

The fluids listed in this table are used for the calibration of the calorimeter. Cp(e) is the experimentally determined value after the calibration is applied, and Cp(1) is the literature value the calibration is based.

Table 2: Cp of Pure Refrigerant

Fluid	Temp. C	Cp(exp) Cp(exp) J/gK	ASHRAE <sup>10</sup>	NEL <sup>9</sup>	Cp(lit) J/kg EOS <sup>4</sup>	SATO <sup>8</sup>	Other
R11	20.5	0.889	0.881	0.889	0.875		0.883 <sup>11</sup>
	37.5	0.897	0.897	0.897	0.891		
	55.5	0.923	0.916	0.922	0.905		0.917
	56.0	0.927	0.916	0.923	0.909		0.917
R22	20.5	1.247	1.235	1.247	1.207		1.226 <sup>12</sup>
	37.5	1.320	1.310	1.320	1.285		
	55.5	1.496	1.448	1.496	1.421		1.449
	56.0	1.500	1.452	1.505	1.427		1.453
Glycol	20.5	2.381		2.381			2.381 <sup>13</sup>
	37.5	2.470		2.470			
	56.0	2.570		2.570			2.566
H <sub>2</sub> O	20.5	4.183					4.183 <sup>14</sup>
	37.5	4.180					4.180
	55.5	4.182					4.182
	56.0	4.183					4.182
R114	20.5	0.982	0.956	0.987	0.991	0.986	
	37.5	1.017	1.040	1.010	1.006	1.016	
	55.5		1.037	1.035	1.028		
	56.0	1.037	1.088	1.036	1.026	1.042	
R123	20.5	0.975		1.080			1.027 <sup>15</sup>
	56.0	1.012		1.095			1.108
R142b	20.5	1.134	1.137	1.204	1.099		
	37.5	1.238	1.230	1.240	1.169		
	55.5	1.308	1.305	1.305	1.251		
R152a	20.5	1.619	1.633	1.695	1.466		
	37.5	1.784	1.811	1.785	1.599		

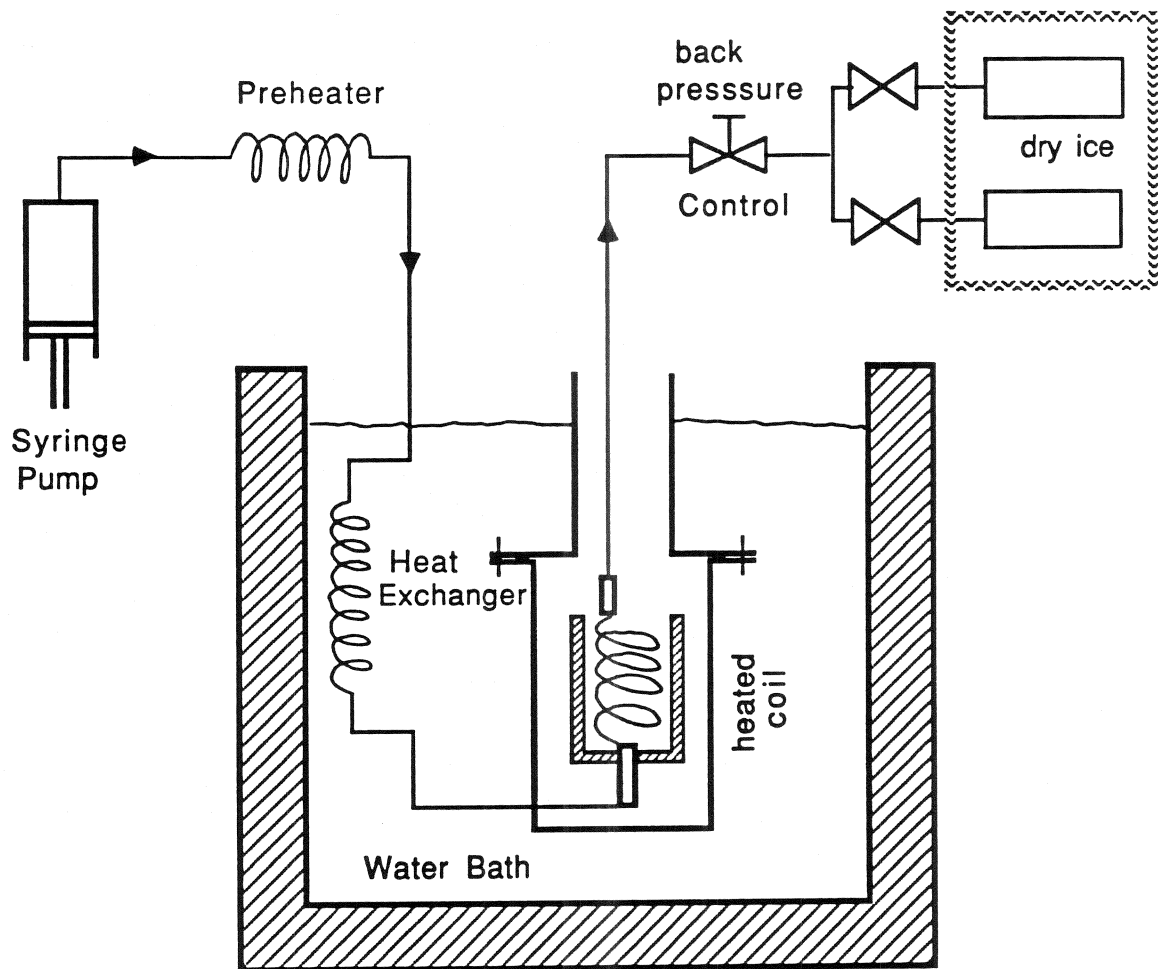
Table 3: Cp of Refrigerant Mixtures

Fluid	Temp C	Concentration g/g	Cp(exp) J/gK	Cp(EOS) J/gK
R22/R114	20.5	20/75	1.026	1.028
		50/50	1.106	1.077
		75/25	1.172	1.137
	56.0	25/75 50/50 75/25	1.114 1.226 1.363	1.104 1.208 1.323
R22/R142b	20.5	24.62/75.38	1.158	1.123
		49.50/50.50	1.192	1.148
		74.58/25.42	1.224	1.176
	55.5	25/75 50/50 75/25	1.344 1.384 1.448	1.273 1.310 1.356
R22/R152a	37.5	27/75 50/50 75/25	1.661 1.541 1.429	1.516 1.434 1.356



### Figure Captions

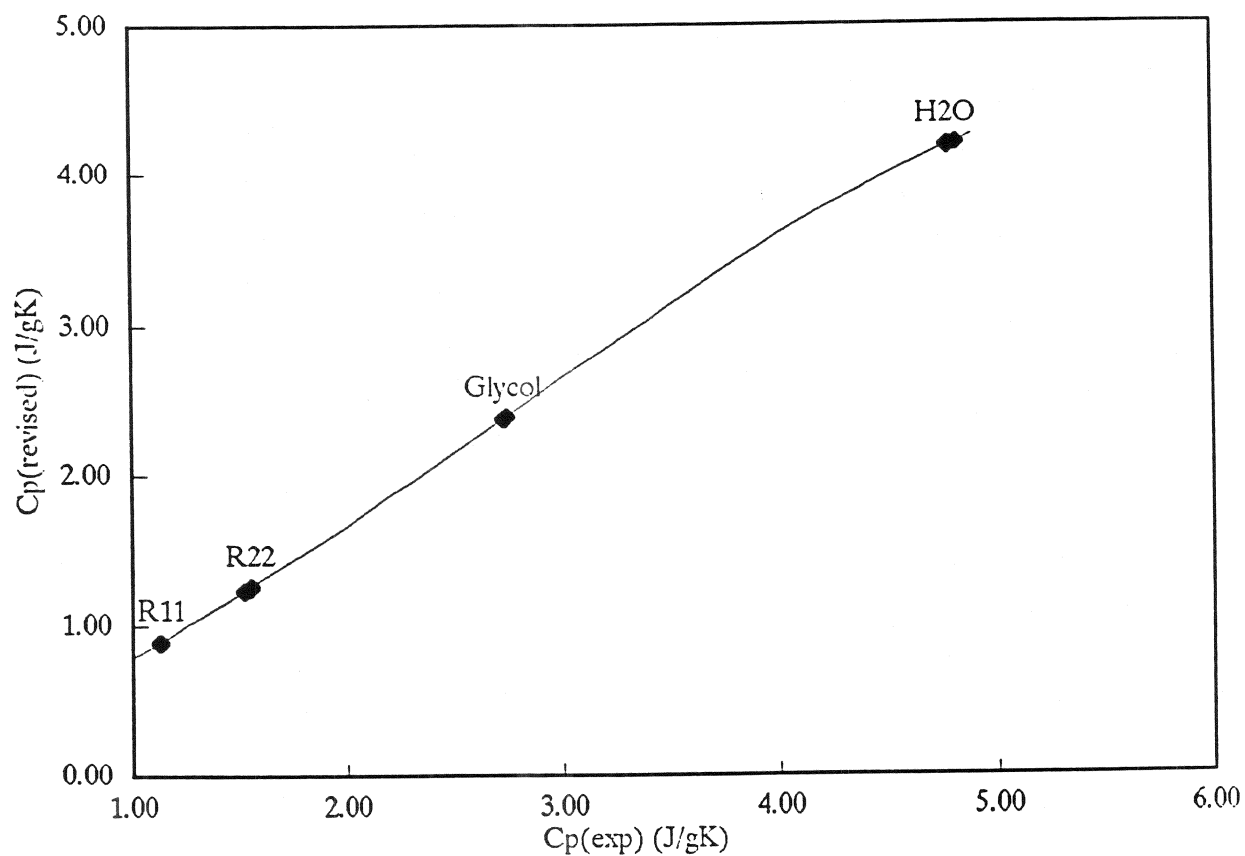
- Figure 1: Schematic of Calorimeter. The fluid under investigation is pumped by means of a syringe pump through two preheaters and the calorimeter cell itself. The cell is located inside a vacuum chamber inside a water bath.
- Figure 2: Calibration curve for the temperature level of 20.5 °C.
- Figure 3: Calibration curve for the temperature level of 37.5 °C.
- Figure 4: Calibration curve for the temperature level of 55.5 °C.
- Figure 5: Calibration curve for the temperature level of 56.5 °C.
- Figure 6: Heat capacity of R22/R114 vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.
- Figure 7: Heat capacity of R22/R142b vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.
- Figure 8: Heat capacity of R22/R152a vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.



Schematic of Calorimeter. The fluid under investigation is pumped by means of a syringe pump through two preheaters and the calorimeter cell itself. The cell is located inside a vacuum chamber inside a water bath.

Figure 1

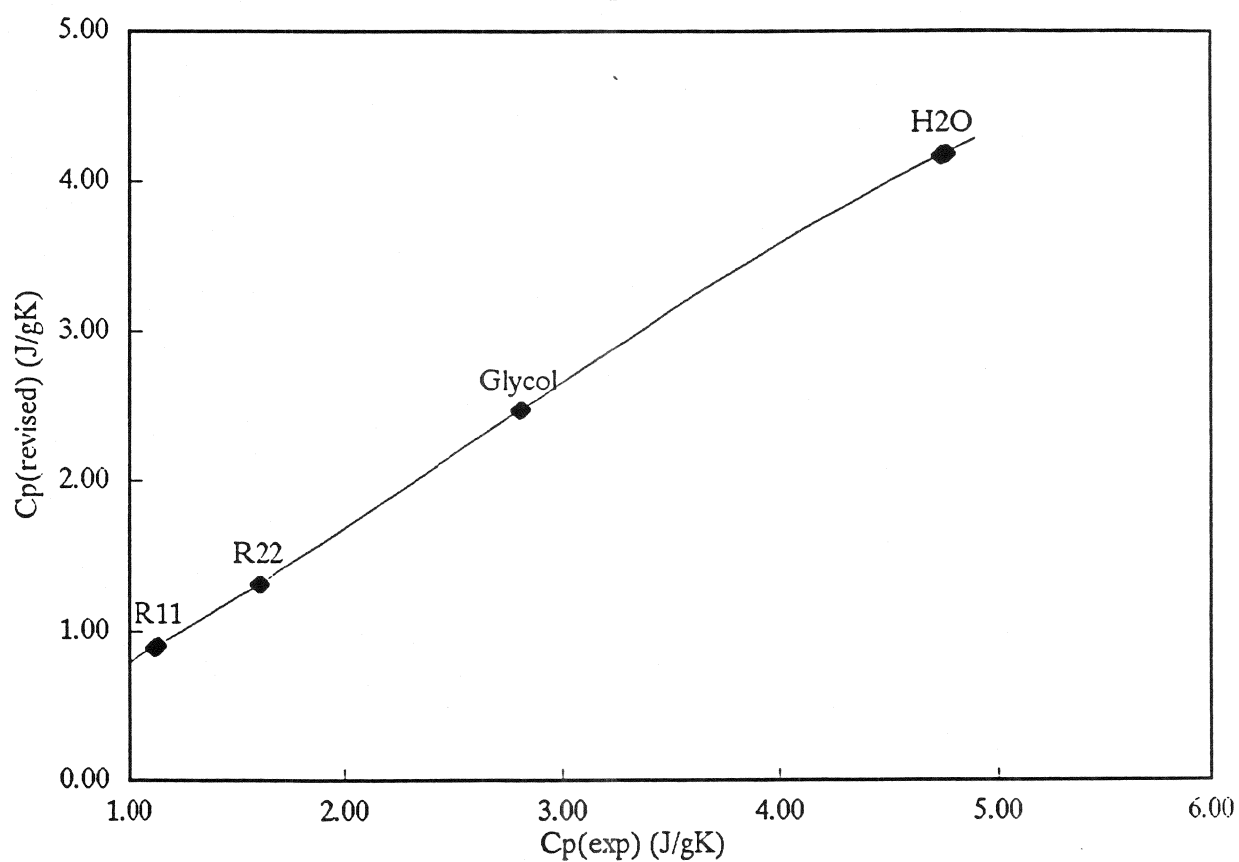
## Calibration of Calorimeter at 20.5 °C



Calibration curve for the temperature level of 20.5 °C.

Figure 2

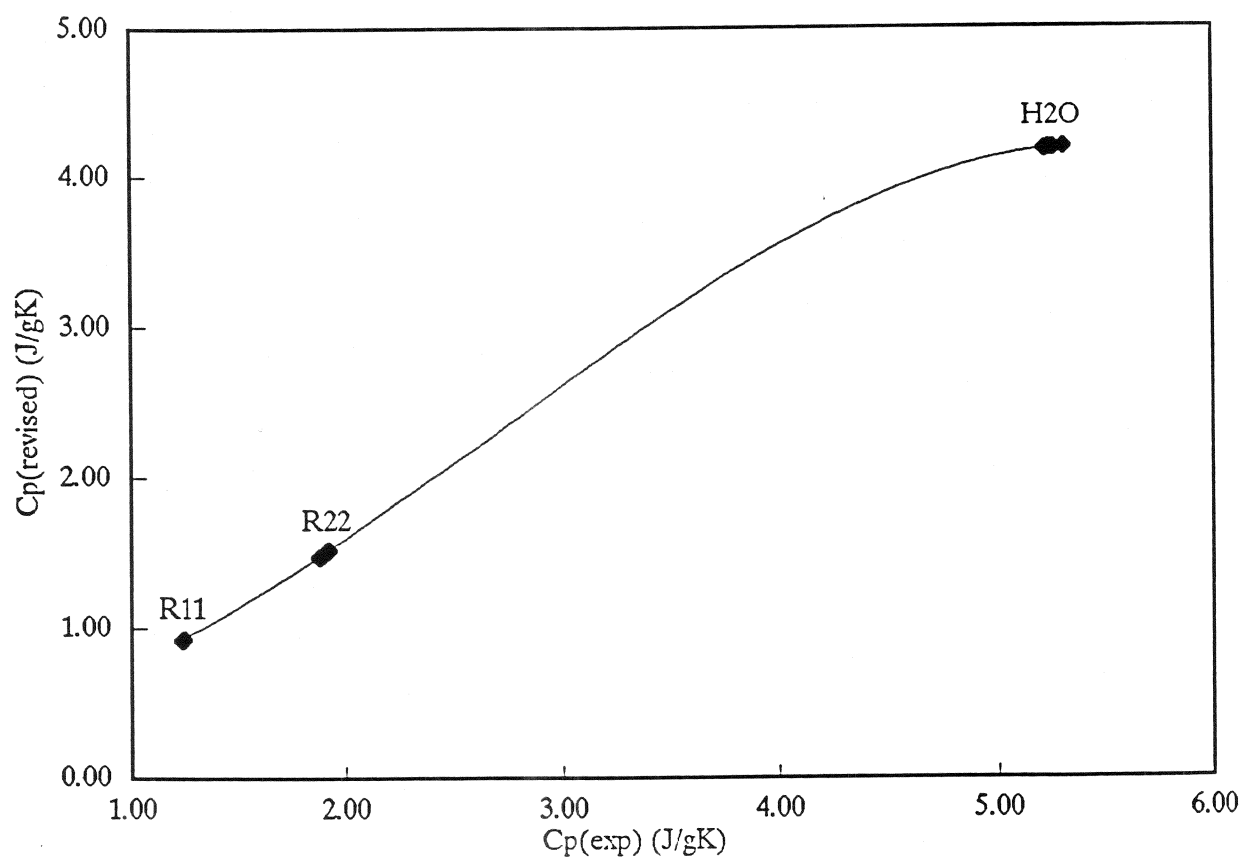
## Calibration of Calorimeter at 37 °C



Calibration curve for the temperature level of 37.5 °C.

Figure 3

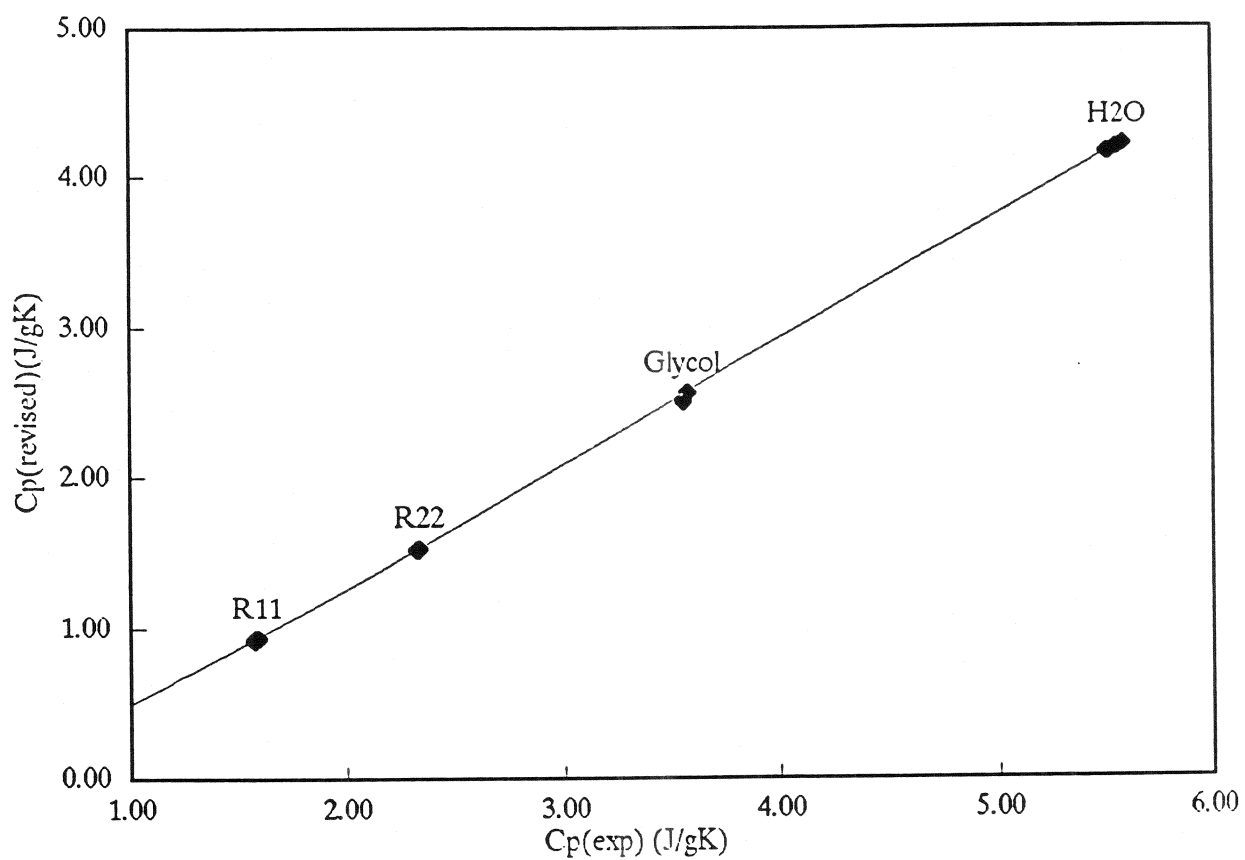
## Calibration of Calorimeter at 55.5 °C



Calibration curve for the temperature level of 55.5 °C.

Figure 4

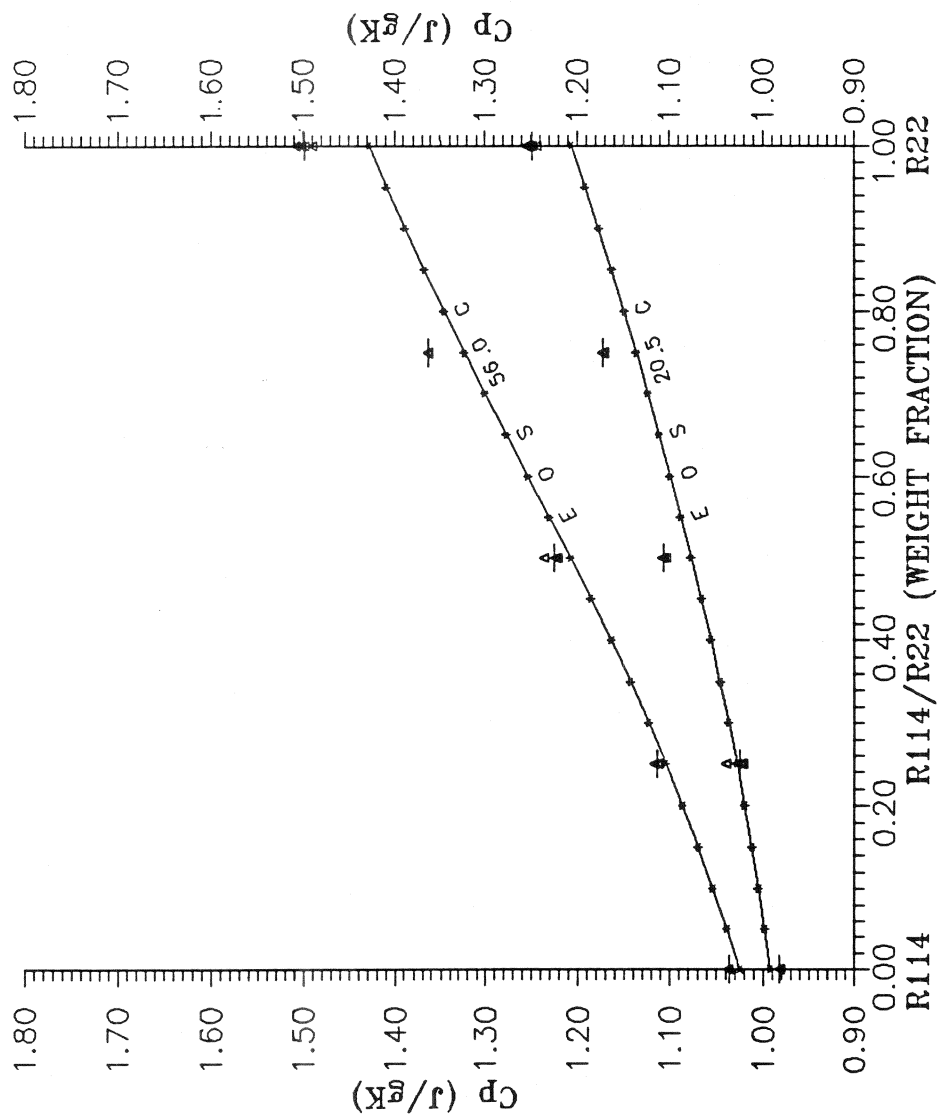
## Calibration of Calorimeter at 56.0 °C



Calibration curve for the temperature level of 56.5 °C.

Figure 5

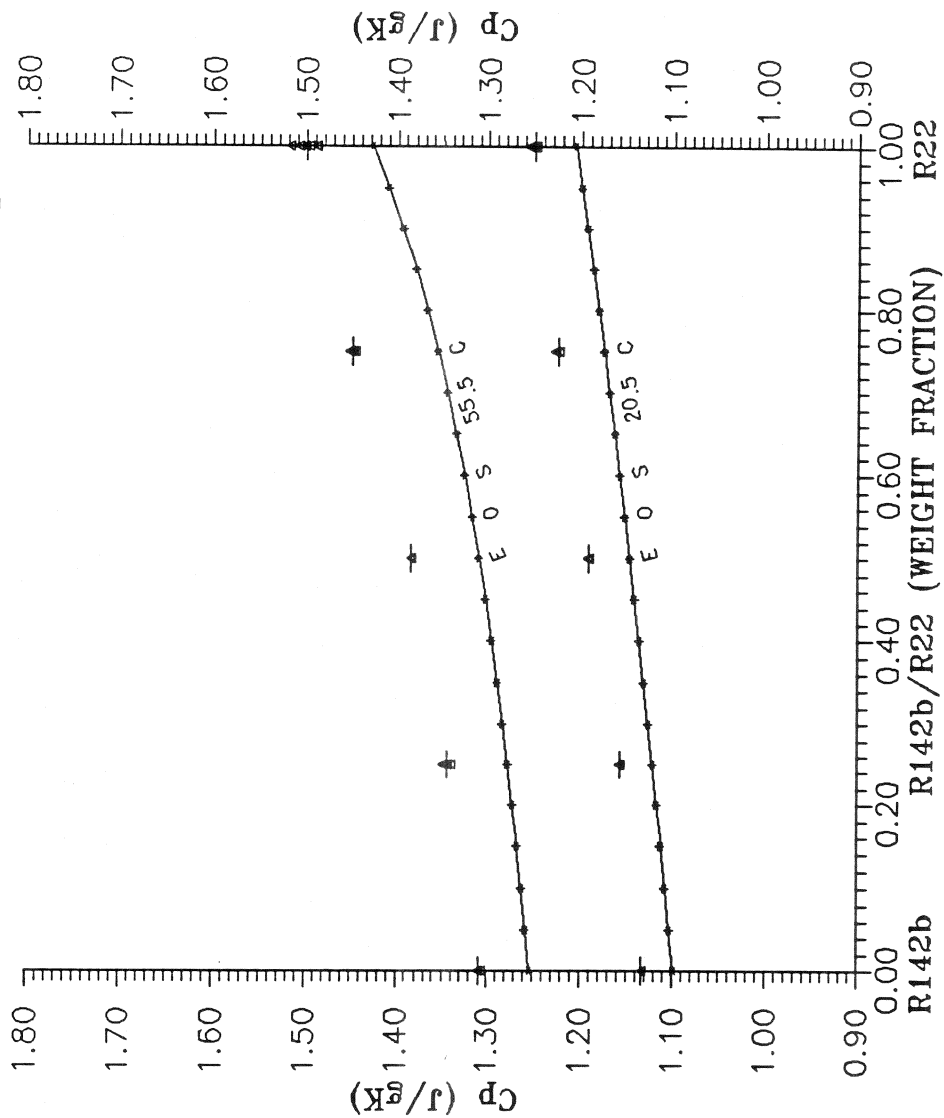
Diagram For Composition & Cp



Heat capacity of R22/R114 vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.

Figure 6

# Diagram For Composition & Cp

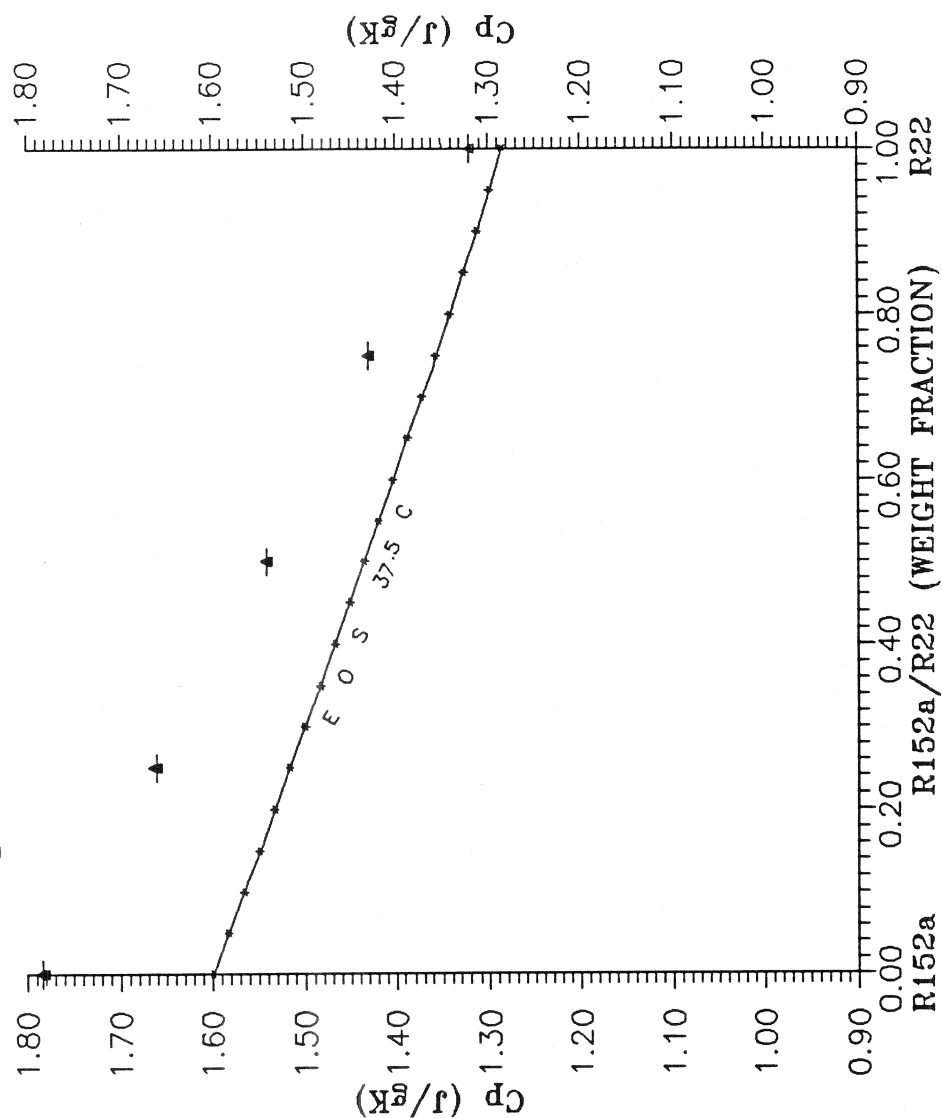


Heat capacity of R22/R142b vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.

Figure 7



# Diagram For Composition & Cp



Heat capacity of R22/R152a vs. weight concentration for two temperature levels. The continuous line represents values obtained from the Equation of State.

Figure 8

